REFRACTORIES

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SERVICE AND PRODUCTION CONDITIONS OF ELECTRO-MELTED REFRACTORY ARTICLES

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The main factors associated with the service of refractories mainly in the melting tanks of glassmaking furnaces are examined. The main technological factors, a description, and the scheme of the technological cycle for the production of refractories at the Domodedovo Plant for Manufacturing Electro-Smelted Articles are presented.

Key words: refractories, glassmaking furnaces, service of refractories, interaction of refractories with molten glass.

In glassmaking the quality of refractory materials is of great importance because it determines the glassmaking capacity, the service life of the glassmaking furnace, and the product quality.

In the overwhelming majority of the cases, commercial refractory articles contain, aside from a high content of a crystalline phase, some amount of a glassy phase. The properties and operating characteristics of refractory materials differ substantially depending on the type and content of the crystalline and glassy phases. The important factors here are the chemical (corrosion) and heat resistance and mechanical strength. As a rule, many flaws in molten glass appear as a result of unforeseen breakdown of refractories during the operation of a glassmaking furnace. This is especially true for electro-melted bacor articles used for the melting tank of glassmaking furnaces, which are subjected to action of the glass melt and high temperatures [1 – 3].

Types of Refractory Materials and Their Application. The refractory articles used in glassmaking are classified as follows:

by chemical composition — alumino-silicaceous (fireclay, high-alumina), silicic (dinas, quartz), corundum, baddeleyite-corundum (bacor), chromium-containing, magnesitic (with additions of Al_2O_3, ZrO_2, Cr_2O_3);

by technological manufacturing method — ceramic, obtained by sintering, and melted, obtained by casting from melts.

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For the elements of the domestic glassmaking furnaces, used in the production of the largest articles from glass (sheet glass, glass containers, dishware, and others), the following types of refractories are used:

bacor — melting tank, channel, and other critical elements;

bacor — burner entrances, elements of the walls of the flame space;

dinas — main crown, elements of the walls of the flame space;

bacor and corundum — outflow channels, feeder channels, drop-forming parts;

magnesitic — hood of the regenerative chambers (top rows).

Service of Bacor Articles in Glassmaking Furnaces. Many factors determine the time period between maintenance for glassmaking furnaces: the properties of the refractories used (heat and corrosion resistance), service conditions of individual elements of the refractory masonry (cooling, insulation), parameters of the technological melting regime (temperature level, extraction of the molten glass, type of fuel, organization of fuel combustion), and structural particulars of the glassmaking furnace.

Reasons for premature breakdown of refractories. First and foremost, these are:

deviation from the rules for optimal arrangement of refractories;

disruption of the heat-engineering regime of the furnace during extraction and operation: global or local temperature rise, sharp temperature differentials, incorrect burning of fuel, excess gas pressure in the flame space of the furnace;

intensified corrosion as a result of chemical – physical processes on individual contact sections of refractory – melt and refractory – steam-vapor phase of the melt; here refractories break down largely because of local chemical interaction between the weakest link in the composition of the refractory and the molten glass and the volatile components of the molten glass; in the contact zone portions of the molten glass which are enriched with Al_2O_3 and ZrO_2 and depleted of Na_2O sink and are replaced by new portions of the molten glass with higher content of Na_2O, lower content of Al_2O_3 and no ZrO_2 (convection under gravity); increasingly deeper layers of the refractory are bared and sections with denser molten glass, enriched with refractory components, and fragments of refractories can remain in the melt, and are a source of flaws in the glass;

the glassmaking temperature and convection flows in the molten glass; an increase of the temperature and intensity of the flows activates chemical and diffusion processes, which intensify when the operation of the glassmaking furnace is incorrectly organized (burning of fuel, blowing, heat-insulation of the elements of the furnace, and others).

Refractories in melting tanks serve under conditions of a stable high-temperature load (1450 – 1550°C) with slowing moving molten glass at the wall and bottom of the tank. Here high glass resistance of the refractory articles and low proneness to separation of bubbles are needed. In the extraction channels and feeders the temperature load is much lower (1300 – 1350°C), and correspondingly the viscosity of the molten glass is higher; the velocity of the molten glass is also much higher than in the melting tank. Under these conditions electro-melted bacor and corundum refractories are most stable. The material of these refractories is least chemically active with respect to the components of the melt.

Aggregate concretions of baddeyelite and corundum crystals are characteristic for the bacor structure; they are largely responsible for the stability of the refractory. At the same time crystallization of a certain amount of corundum, not bound in aggregate concretions with baddeyelite, is seen. Such crystals interact more easily with the molten glass and weaken the refractory.

The breakdown of bacor and the formation, on this basis, of flaws in the glass occur as a result of the combined effect of high temperature and chemically active molten glass. An analysis of the service of the refractory materials and the particulars of their breakdown under real operating conditions of the tanks of glassmaking furnaces is presented in [4].

Interaction of the molten glass with refractories. The constituent parts of a refractory which possess substantially different resistance to a corrosive molten glass break down differently, and the glass phase plays the main role in these processes. Reactions occur between the glass phase of the refractory and the molten glass, and as a result the silica content becomes more even, the composition of the contact medium shifts into the region of the higher-temperature eutectics, and the prerequisites appear for the formation of alkali aluminosilicates. The differential character of the breakdown of bacor helps to weaken its phase-structural bonds, especially in the baddeyelite – corundum mineral concretions and the binder of the glass phase. As a result not isolated minerals but rather small volume fragments of refractory can enter the molten glass. These fragments and the molten glass with an elevated content of ZrO_2, which are denser than the molten glass having the main composition, can accumulate in the bottom layers of the melting tank of a furnace. The change in the character of the motion of the flows of molten glass, caused by an increase in extraction, diathermancy, or other reasons, can cause these concretions to enter the product flow and result in the appearance of numerous flaws in the form of scale and striae. An example is the formation of zirconium striae in glass containers; the source of the striae is corrosion of the walls of the melting tank, the bars of the pouring threshold, the cover bars of the channel, and the bacor elements in the top structure of the furnace [5].

Diffusion phenomena play a considerable role in the interaction of molten glass with refractories [3, 6, 7]. The entire volume of the high-viscosity melt in the glassmaking furnace can be conventionally divided into three regions:

the region of the main bulk of the melt, where the concentration of the dissolved matter of the refractory is negligible compared with the saturation concentration;

the region of a constant distribution of the concentration and convection diffusion at a definite distance from the surface of the refractory — a hydrodynamic boundary layer; here the flow is laminar and melt viscosity plays the main role;

the region of rapid change of the concentration and with diffusion of ions directly near the surface of the refractory material — a diffusion layer; here the saturation concentration is reached, and for highly viscous glass melts enriched with refractory components this layer can be regarded as strongly bound to the surface of the refractory.

The process of breakdown of the refractory intensifies as the melting temperature and the specific extraction of the molten glass increase. The temperature factor, which intensifies the chemical interaction between the refractory and the molten glass, plays the decisive role here [4]. Under the action of the flows of molten glass, especially on sections where the flows undergo intense mixing, diffusion phenomena intensify and the products of the interaction of the refractories with the molten glass via convective diffusion are more actively transferred from the diffusion layer into the main volume of the melt through the hydrodynamic layer. So, the threshold and cover bars of the channel as well as the wall bars of the tank at the level of the surface of the molten glass are subjected to strong breakdown. In the latter case a unique, small cap appears on the refractory; drops of viscous molten glass can flow off this cap and form alumina and zirconium-containing streaks and bundled striae, sometimes with secondary crystallization in the form of alkaline alumino-silicates or baddeyelite. The bacor elements of the top structure of a glassmaking furnace can be a source of the zirconium streaks because of the “sweating out” of the glassy phase of bacor, containing up to 20% Al_2O_3 and up to 6% ZrO_2 [5].

Data from many examinations of the state of the refractory masonry of the tanks of glassmaking furnaces for the production of the most massive articles show that, as a rule, the service life of furnaces is limited not by a general unsatisfactory state of the entire refractory masonry but rather by the breakdown (often accidental) of a limited number of structural components of the melting tank and the flame space in the melting and maximum temperature zones. On this basis it is necessary not only to use highly resistant refractory materials but also to approach the operation of a glassmaking furnace knowledgeably.

The generalized results of the service of refractories in the tanks of glassmaking furnaces under real operating conditions are briefly presented below.

The walls of the melting tank are most often the main link limiting the service life of a glassmaking furnace, especially if the quality of the refractories is low. Corrosion of the walls of the melting tank at the level of the surface of the molten glass, at the interface of three phases, often results in the refractories at this location completely wearing out. Statistical analysis of the results performed at a number of plants established that the main factors influencing the corrosion of electro-melted bacor refractories are the glassmaking temperature and the specific extraction of the molten glass [4]. An increase of the glassmaking temperature has a much larger effect than an increase of the specific extraction of molten glass, especially since the velocity of the glass mass near the walls of the melting tank does not exceed 10 m/h. The effect of the extraction of molten glass is related not with the mechanical action on the refractory but rather with the rate of removal of the products of interaction from the reaction zone (the diffusion layer) into the bulk of the moving melt through the hydrodynamic boundary layer.

The main factor in long-time of operation of a glassmaking furnace is the use of high-quality refractories. At the same time cooling the appropriate sections of the refractory masonry, for example in the top row of wall bars at the level of the surface of the molten glass and the bars in the channel, increases the viscosity of the glass in the contact zone and, correspondingly, decreases the diffusion coefficients.

Cover bars of the channel. The quite high degree of corrosion is due to the high temperatures (active chemical interactions) and the velocities of the molten glass (intensification of the diffusion processes) combined with the vertical cellular corrosion by gas bubbles [1, 2]. To a significant extent the corrosion of the cover bars of the channel can be decreased by air cooling and inclining the bars.

Top bars of the pouring threshold. The corrosion of these elements of the tank of a glassmaking furnace is due to a combination of high temperature in this zone and comparatively high velocities of the molten glass. This pertains to the main production flow and convective flows, including convection under gravity, at the side surfaces. The intense motion of the molten glass intensifies diffusion phenomena by decreasing the thickness of the diffusion layer.

The bottom of the melting tank is not a limiting element for the service life of a glassmaking furnace provided that elementary rules are followed for the masonry and that high-quality refractories are used. It should be noted that the use of a multilayer heat-insulating bottom has a number of advantages. Such a bottom is characterized not only by high operational reliability but also the possibility of smoothing the temperature gradient along the depth of the melting tank, increasing the chemical and thermal uniformity of the molten glass, and fuel savings.

Production of Bacor Refractories. The process of manufacturing electro-melted bacor refractories is distinguished by its complexity and controlled multistage nature and includes preparation of the initial materials, preparation of the mix, high-temperature melting, casting of articles, heat treatment (annealing) and mechanical working (cleaning, cutting, grinding), a customer-determined stand assembly, packing, and shipment.

Main technological factors. These factors affect the quality of refractory articles and therefore their reliability during the operation of a glassmaking furnace. They include the following:

the composition of the refractories; when choosing the composition it is necessary to know the conditions of service of the glassmaking furnace; the most severe conditions are observed in the melting part of the furnace (top part of the wall bars at the level of the surface of the molten glass, burner entrances, and channel);

the quality of the initial materials, including bacor scrap; the materials used should not contain harmful impurities, the content of iron oxides must be reduced to a minimum;

the quality of the mix preparation; the mix composition must correspond quite accurately to the prescribed composition of refractories; comminuted materials with a definite granulometric composition with no iron impurities from apparatus should be used to make the mix;

the mix melting regime; the final objective of melting the mix is to obtain a uniform melt with a prescribed chemical composition, a definite temperature, and good pouring qualities; the melting process is regulated by amount of mix and scrap loaded, the character of the gas medium in the working space, the change of the electrical parameters (voltage, current strength, power); appropriate regime parameters must be developed to satisfy these conditions;

the regime of casting the melt; the final objective of casting is to obtain from the melt a block with prescribed dimensions and a dense structure and good operating characteristics; the temperature of the melt, the material used for the molds and the time required to fill the molds, the method of filling the molds, the pouring properties of the melt (flowability, shrinkage, pouring time, and others) are the main factors determining the size, structure, and characteristics of castings;

the heat-treatment regime for electro-melted refractories has a decisive effect on their quality; as the melt solidifies, a zonal structure of the refractory forms and the regime of cooling of the solidified casting affects the magnitude of the thermal stresses arising in it, which under certain conditions can lead to the formation of dangerous cracks.

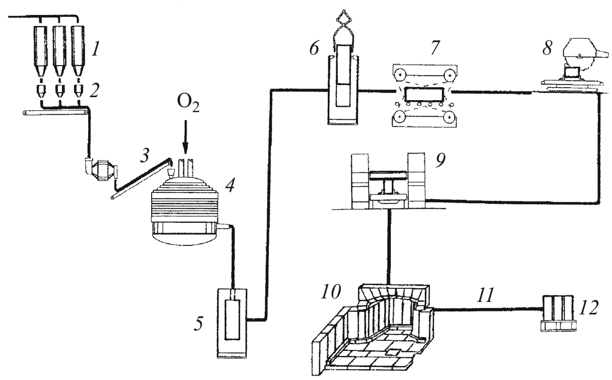

Fig. 1. Schematic diagram of the technological production cycle for electro-melted refractory articles: *1*) prepared initial materials; *2*) weighing; *3*) mixing (mix preparation); *4*) melting in an electric furnace; *5*) casting refractory articles; *6*) annealing and extraction of refractory articles; *7*) cleaning by sandblasting; *8*) cutting; *9*) grinding; *10*) stand assembly; *11*) final inspection) production and by the customer; *12*) packing and shipment of refractory articles.

The manufacturing conditions for large bacor bars are such that the bars inevitably contain sections with chemical and phase-structural nonuniformity, manifested in fluctuations of the content of zirconium dioxide, alumina, silica, and impurity oxides. Over the thickness of a bar these indicators are characterized by zonality. The working surface is distinguished by a dense fine-grain microstructure, contains an elevated amount of ZrO_2 with a decrease of the lower content of silica and impurities. Thermal and chemical strength of this surface is highest.

Production of Refractories at the Domodedovo Plant for Electro-Melted Articles. The plant was built and began operations in 2002. It specializes in the production of electro-melted high-quality refractory articles for glassmaking furnaces: bacor bars with normal and high density; corundum refractory articles; bacor and corundum refractory powders.

A schematic diagram of the technological production cycle for refractory electro-melted (bacor and corundum) articles is presented in Fig. 1.

The prepared initial materials — highly pure oxides — are weighed and fed into a mixer and then into an electric melting furnace with oxygen supplied to oxidize the impurities. After the technological melting stage the refractory articles are poured into special molds, which are prepared in parallel with the main technological process. The cast refractory materials are annealed. The annealing process is carefully controlled in order to obtain the required material structure and texture for the articles taking account of the service conditions and ensuring a long service life for the corresponding units in the glassmaking furnace.

Next the articles are extracted and mechanically worked: cleaning, cutting, grinding. Each article is worked with strict dimensional tolerances so that the maximum accuracy is attained and speed of assembly of the refractory masonry of the glassmaking furnace. After the treatment operations have been completed, stand assembly of the masonry elements of the glassmaking furnace is performed, followed by a final production check and check by the customer. Then the refractory articles are packed and shipped to the customer.

It should be noted that the process parameters and production quality are carefully monitored at all stages of the technological process.

Work to increase the quality of refractory articles is continually being performed at the plant. A great deal of attention is given to obtaining a dense uniform structure and texture of the working zone of refractory articles, which are characterized by the formation of a densely connected framework of baddeyelite and corundum with the lowest possible porosity and a uniform distribution of the glass phase in a thin layer.

The refractory articles of the Domodedovo plant successfully served in glassmaking furnaces and feeders in many plants in Russia (Kamyshin, "Krasnoe Ékho," Bun'kovo, Klinsteklotara, Dmitrovsteklo, "SOLSTEK," and others). Refractory articles from the Domodedovo plant have been operating successfully for more than six years in a number of glass enterprises. If the customer wishes, the plant can fabricate nonstandard refractory articles.

The main directions of the work done by the plant staff is high quality and reliable operation of refractory articles.

To increase the operational efficiency of glassmaking furnaces in glass plants not only is it necessary to use high-quality electro-melted refractory articles but the operation of the furnace must be approached knowledgeably.

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